

Argonne National Laboratory

**SOME FUNDAMENTAL ASPECTS
OF VAPORIZATION**

by

**R. J. Ackermann, R. J. Thorn,
and G. H. Winslow**

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TABLE OF CONTENTS

	<u>Page</u>
I. INTRODUCTION.	3
II. GENERAL FORMULATION OF PROBLEM	5
III. SOME EQUILIBRIUM RELATIONS.	8
IV. IRREVERSIBLE CHARACTER OF EVAPORATION	12
V. SUMMARY	23
REFERENCES.	25

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I. INTRODUCTION

For decades it has been recognized that the rate at which a substance evaporates into an evacuated space may be less than the rate at which its equilibrium vapor impinges upon the surface of the condensed phase, even though both are at the same temperature. In fact, the assumption that the evaporation rate of a metal is given by the kinetic theory expression for the number of molecules striking a unit area in unit time is, logically speaking, more of a convenience introduced as a plausible postulate than a deduction. Because of experimental difficulties, a general and precise confirmation still is lacking or is available only to limited precision (a few per cent) or is available for only a few materials.

Numerous studies⁽¹⁾ have demonstrated that for many substances under certain conditions the rate of evaporation is only a fraction of the saturation rate. Several discussions have introduced a posteriori explanations for the existence of a non-unit vaporization coefficient. Some of these associate the phenomenon with experimental difficulties;⁽²⁾ others, of course, are of a more recondite nature. It is primarily the latter which are the topics of this paper. But we must recognize that both result from an incomplete knowledge of the system.

The writers believe that the time has come to take some sharply defined step away from attempts to explain vaporization, condensation, and accommodation coefficients in terms of equilibrium theories modified in the usual way. It is the present intent to discuss briefly what is definitely known about the fundamental aspects of vaporization, to discuss evaporation within the concepts of existing theories of solids and gases, to suggest where assumptions might be introduced to describe the phenomenon more completely, to attempt to define those factors which can give rise to vaporization coefficients, and to attempt to unify these within the phenomenological framework of irreversible thermodynamics.

There are a few representative sources to which one can refer for a review of the subject of vaporization. Some of these are mentioned here only briefly, since the present discussion is a supplementary commentary rather than an exhaustive review. The studies of Langmuir⁽³⁾ and of Lennard-Jones and his associates⁽⁴⁾ illustrate clearly the fact that condensation in general must be discussed and explained in terms of the forces or, perhaps

preferably, the potentials between gaseous atoms and surface atoms. Thus, the rate of condensation and the fraction condensing depend on the shapes of these potentials and upon the energies of the incoming particles. (Under the general phrase "shapes of these potentials" it is meant to include the effect of electron-exchange interactions.) For example, a potential with a maximum - an activation energy - between the high-energy region outside the solid and the lower-energy region in or on the solid will cause the reflection of those particles which approach the surface with low kinetic energy. Particles which approach with sufficient energy to surmount such a barrier will be trapped only if there is a mechanism which will hold the particle long enough to allow the excess energy to be dissipated through the lattice and if the necessary transitions between quantum states are allowed. It should be noted that the potential seen by a particle which approaches a surface of a different chemical composition will, in general, be altered by the near presence of a similar particle. Thus, while the attachment of a single particle to a surface may be improbable, sufficient density in the gas phase can initiate nucleation⁽⁵⁾ via such potential alterations. This necessitates then a critical vapor density for the nucleation of condensate on a "nonattractive" substrate. If a strong attraction between gas and substrate exists, then the critical vapor density must be defined in terms of the free energy of a monolayer. Since Langmuir's principal interest was in the behavior of monolayers, his primary contribution to interphase transfer is a recognition of the fact that, in general, the process of condensation from its inception may pass through the regions of monolayers, multilayers, and, finally, to a surface characteristic of the condensed phase. In this sequence the potential energy between the gaseous particles and the surface is changing.

Prüger⁽⁵⁾ has emphasized the distinction which must be delineated between accommodation and condensation coefficients, and has suggested how they may be interrelated. In an analysis of the "kinetic consideration of vaporizing substrate" he has demonstrated that no statement concerning the value of the condensation coefficient can be made on the basis of such general [kinetic] considerations. Schrage⁽⁶⁾ has discussed interphase mass transfer entirely from a gas kinetic viewpoint, which again does not yield any information concerning the origin of the vaporization or condensation coefficients; that is, while Schrage shows the role played, for instance, by the condensation coefficient, he throws no light on the reason for there being such a coefficient with a value less than unity.

Knacke and Stranski⁽¹⁾ have reviewed several of the experimental attempts to measure vaporization coefficients. In addition to the usual kinetic or statistical theories reviewed by Prüger, Knacke and Stranski discuss to some extent the use of partition functions and, in particular, that of the activated complex. Some of the grosser aspects of evaporation are elucidated by the stepwise theory of evaporation by which the following sequences occur: "Half-crystal position \rightarrow step \rightarrow surface \rightarrow vapor." As shown by Knacke and Stranski, this treatment yields no particular information about the vaporization coefficient other than an estimate that it is

approximately unity. The kinetic model developed by Hirth and Pound⁽⁷⁾ has demonstrated the role of surface-diffusion effects in producing nonunit vaporization coefficients.

As much as possible it is desirable to attempt a unified discussion which encompasses all of the factors which are known to produce a vaporization coefficient different from unity. These are temperature gradients, composition gradients, surface energies, frozen internal states in molecules and atoms, and surface contamination. A method of attack which heretofore has not been emphasized and which is an important one, since it serves as a critique for all kinetic considerations, is provided by the concepts of irreversible thermodynamics.

II. GENERAL FORMULATION OF PROBLEM

The process which is to be discussed herein is one in which evaporation of a single component occurs into an evacuated space from a surface where the pressure of the vaporized gas is such that the mean free path is greater than some appropriate dimension descriptive of the surface irregularities. Since most feasibly effected experimental observations of this process measure the net flux of matter, J_m , at a distance from the surface large compared with the surface irregularities, one is interested principally in a discussion involving this quantity. For theoretical reasons, on the other hand, it is valuable to include, also, gross rates of transport away from and to the surface as will be done later. Before doing this, however, it is desirable to point out that no discussion of the evaporation process can be considered complete unless the flow of heat, J_{th} , through the surface is also included, because, as will be shown later, the mass and heat fluxes are intimately related. The omission of the heat flux from previously presented studies has limited severely the interpretations given; we are aware of only one attempt to include it. Littlewood and Rideal⁽²⁾ considered briefly its effect on the vaporization process, although not from an irreversible thermodynamic viewpoint.

To some extent, confusion has occurred because of inadequately understood definitions of vaporization, condensation, and accommodation coefficients, and a tendency to use them interchangeably. The need for a careful definition of these terms, particularly with respect to temperature relationship, is illustrated somewhat by the following paradox which results from an incomplete understanding of them. One can show that at equilibrium the vaporization coefficient must equal the condensation coefficient. Therefore (one might argue), if the vaporization coefficient decreases monotonically with decreasing temperature, the substance cannot be condensed by decreasing the temperature. Or, if the vaporization coefficient increases monotonically with decreasing temperature, as observed by Littlewood and Rideal⁽²⁾ for phenanthrene, and by Trick and Rideal⁽⁸⁾ for benzophenone,

then it must approach unity at low temperatures and zero at high temperatures, so that a (high) temperature may be attained such that vaporization ceases.

Since substances do not behave this way one seeks the errors which lead to these paradoxes. One resolution is to postulate that the vaporization coefficient has a minimum value at some temperature and approaches unity at high and low temperatures. It appears, however, that this "explanation" is evasive and, hence, is not particularly informative. There is another which is intimately associated with the interrelations among the three coefficients, and which has been mentioned earlier. Although it is necessary that the vaporization coefficient must equal the condensation coefficient if the gas and condensed phases are at equilibrium, nothing requires that they be equal if the gaseous and condensed phases are at different temperatures. Further, not only does the vaporization coefficient equal the condensation coefficient (at equilibrium), but both essentially lose their intrinsic meaning because it is impossible to distinguish between reflected and emitted atoms at equilibrium. On the other hand, it is of no importance to be able to do so at equilibrium.

In the construction of a schematic representation of the vaporization process, the following suggestions should be followed as representational of the lessons taught by previous work:

1. Eventually, the discussion from the point of view of solid state theory, as well as gas kinetic theory, will have to be extended beyond the work of Lennard-Jones and his associates.⁽⁴⁾

2. The nonequilibrium coefficients should not be introduced into equilibrium statistical mechanical equations after they have been derived because (a) inconsistencies are created and (b) the introduction a posteriori of the coefficients does not in general provide an insight to their source.

It is important, then, to give definitions of these coefficients which will reflect properly the ideas stated in the preceding paragraphs. The definitions must make sense experimentally, also. The authors realize that the ones to be given are a posteriori in the sense that they are formulated after an unexpected event, namely, an event typified by a lack of agreement between observed evaporation rates and those calculated from vapor pressure data. Proper a priori definitions would be based on an atomistic model so that the effects of a (possible) non-Maxwellian velocity distribution, for example, could be included. On the other hand, the definitions given here are illustrative of every aspect of the problem except the possible inability, which would be associated with the velocity-distribution problem, to assign certain temperatures rigorously.

Let G_{Os} represent the rate of particle flow produced by one cm^2 of surface when the material evaporates at the equilibrium rate. Thus,

$$G_{Os} = n_s \bar{c} / 4 = P_s / (2\pi m k T_s)^{1/2} \quad , \quad (1)$$

where \bar{c} is the average speed of the evaporating molecules, T_s is the temperature of the surface, the subscript s on P_s , n_s , G_{Os} refer to saturation and, otherwise, the letter designations have their usual meanings. The reader must be warned about one possible source of confusion in Eq. (1), which would arise because of the nature of some of the emphasis being attempted in this paper. Equation (1) should not be construed to mean that the right side (the rate of incidence on the surface from the saturated gas) is a functional expression for G_{Os} . The latter would have to contain properties of the condensed phase. Rather, the right side of Eq. (1) merely allows the determination of the numerical value of G_{Os} . This procedure is an illustration of the convenience mentioned in the first paragraph of this paper.

Similarly, let $G_i (P, m, T_i)$ represent a rate of impingement on this surface.⁽⁹⁾ Let J_m represent the net flow away from the surface. Let α_e be called the vaporization coefficient and let α_c be called the condensation coefficient. Then the defining equation which relates these quantities is

$$\begin{aligned} J_m &= \alpha_e G_{Os} + (1 - \alpha_c) G_i - G_i \quad , \\ &= \alpha_e G_{Os} - \alpha_c G_i \quad . \end{aligned} \quad (2)$$

It will be clear that no progress can be made, regardless of the nature of the definitions of these coefficients, unless it is possible to determine G_{Os} . This can be done by means of Eq. (1), for instance, if an a priori knowledge of P_s is obtained from some source other than a Langmuir experiment or a "too carelessly" designed effusion experiment. Once this has been done, α_e can be determined by an evaporation experiment, such as the Langmuir experiment, in which G_i is zero. Then, when G_{Os} and α_e are known, G_i can be (experimentally) established as desired and J_m measured, in order to determine the particular α_c of interest.

It is illustrative to mention a few special cases. If incoming atoms are being (partially) condensed on a nonevaporating substrate, $G_{Os} = 0$ and J_m , the net flow away from the substrate, will be negative. Its absolute value will be the rate of condensation and the ratio of it to the incoming rate will be the condensation coefficient, $\alpha_c (T_{\text{gas}}, T_{\text{substrate}})$.

If G_{Os} and G_i represent the same sort of particles, but at different temperatures, and if it has been determined that α_e is unity at the temperature T_s of the surface, then

$$\alpha_c (T_i, T_s) = G_i^{-1} (G_{Os} - J_m) \quad .$$

Finally, in an equilibrium situation, $G_{os} = G_i$, and $J_m = 0$. Equation (2) then says that $\alpha_e = \alpha_c$, but gives no information about specific values of either. The definitions of α_e and α_c are, therefore, consistent with the contention that both lose their intrinsic meaning at equilibrium and can never be measured in a truly equilibrium experiment.

The greatest confusion arises in the definition of the accommodation coefficient a , a situation which has not been helped by the occasional use of this term to mean the vaporization or condensation coefficient. The accommodation coefficient was originally defined for a case⁽¹⁰⁾ (Knudsen's absolute manometer) in which there was no net condensation (at least after a steady state was reached). It is in similar work, as in the heat conductivity of dilute gases, where it is still principally used. The accommodation coefficient is a useful concept in the present case also, but careful definition should be made. If E_i is the energy brought up to a surface by that part of the impinging gas that is going to be "reflected," E_r that carried away by the "reflected" gas, and E_s the energy with which fully accommodated molecules escape from the surface, then

$$a = \frac{E_i - E_r}{E_i - E_s} \quad (3)$$

It is clear that this definition will involve the same quantities as would appear in the condensation coefficient, with the additional consideration of the energies, kinetic and potential, carried by the particles.

III. SOME EQUILIBRIUM RELATIONS

Both the Einstein and the Debye theories of the solid state are based upon the concept of the harmonic oscillator and consequently do not in themselves provide a mechanism for evaporation. Lennard-Jones et al.,⁽⁴⁾ worked with a Morse potential at the surface of a Debye solid. Such a potential

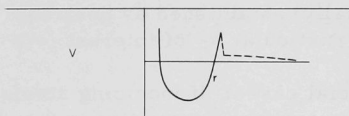


Fig. 1. Schematic Representation of the Potential Energy of a Modified Harmonic Oscillator Which Will Dissociate or Evaporate

does allow evaporation to occur, but much extension of their work is necessary. For instance, it might be desirable to consider a solid which has a potential energy curve which recognizes that the oscillators in the surface are different in number and frequencies than those in the interior. On the other hand, it is very likely that much could be learned by exploration of all the implications of a simpler potential energy function of the type sketched in Fig. 1. If this is done,

a simple means to permit vaporization has been provided in that the harmonic oscillator is cut off by a "condensation" barrier.

In the following discussion, two limited aspects of the evaporation of the Debye solid are outlined briefly. First, an attempt is made to show how the theory leads one to some information about G_{OS} and α_e ; secondly, there is cited one particular difficulty with current attempts to introduce rate concepts into equilibrium theory. The nature of the difficulty is such that application of the principles of irreversible thermodynamics to the problem is more profitable as a next step, rather than the use of a new departure within the framework of the equilibrium theory of absolute reaction rates.

The equilibrium-rate aspects of the vaporization of a Debye solid can be described, superficially at least, as follows. For a harmonic oscillator there are two extreme positions per vibration. However, attention is to be centered on the number of atoms that might leave the surface per second. Reference to Fig. 1 shows that it is unlikely that both of these positions should be considered as possibilities from which separation could ensue. Hence, only ν extreme positions for the ν vibrations per second will be counted.

For a Debye distribution of oscillators⁽¹¹⁾ there are

$$N(\nu)d\nu = \frac{9N}{V} \frac{\nu^2}{\nu_m^3} d\nu \quad (8)$$

possible modes of vibration per unit volume in the frequency range between ν and $\nu + d\nu$, where V is the crystal volume, N is the number of atoms therein, and ν_m is the largest frequency. Hence, there are

$$\nu N(\nu)d\nu = \frac{9N}{V} \frac{\nu^3}{\nu_m^3} d\nu \quad (9)$$

extreme positions per unit volume per second in the range between ν and $\nu + d\nu$. The total number of extreme positions per unit volume per second is

$$\frac{9N}{V\nu_m^3} \int_0^{\nu_m} \nu^3 d\nu = (9/4)(N/V)\nu_m \quad (10)$$

Of these, one can assume that a fraction f will produce configurations such that bond rupture can occur. If the surface is taken to be some region of thickness τ , then the number of atoms per unit area which are favorably oriented is

$$(9/4)(N/V)\nu_m f \tau \quad (11)$$

Of these, only the fraction $\exp [-\lambda/(kT)]$, roughly, have sufficient energy λ to rupture the bond and evaporate. Hence, if θ is the Debye temperature, the evaporation rate is

$$\alpha_e G_{Os} = f(9/4)(N/V) \exp [-\lambda/(kT)] (k\theta\tau/h) \quad (12)$$

If the rate of incidence onto the surface is the saturation rate, then

$$G_i = G_{Os} = 1.013 \times 10^6 (2\pi mkT)^{-1/2} \exp(\Delta S^\circ/R) \exp[-\Delta H^\circ/(RT)] \quad (13)$$

At equilibrium, for which $J_m = 0$ and $G_i = G_{Os}$, it was shown earlier that $\alpha_c = \alpha_e$. If, at this point, however, one only applies to Eq. (2) the condition $J_m = 0$, he can obtain an expression for α_c . Thus, $\alpha_c (= \alpha_e)$ is given by the right side of Eq. (12) divided by the right side of Eq. (13). Consequently, it is natural to associate λ/k with $\Delta H^\circ/R$, where ΔH° is the heat of vaporization. If, for example, one uses a molecular weight of 25, $T = 1600^\circ K$, $\theta = 300^\circ K$, $\Delta S^\circ = 25$ eu, and 5 gm cm^{-3} as the density of the solid, one obtains the result

$$\alpha_c = \alpha_e \approx 5 \times 10^7 f\tau \quad (14)$$

for τ in cm.

This is a very reasonable result in that it associates f with the vaporization and condensation coefficients, and it agrees with the correct orders of magnitude, $\alpha_c = \alpha_e \sim 1$, $f \sim 1$, and $\tau \sim 10^{-8} \text{ cm}$. Actually, f would be expected to be less than unity; that is, it is not likely that every direction of motion which has a component of velocity toward the gas phase is equally likely to lead to separation. For instance, even if one retains the present simple harmonic oscillator model, he must expect that particles moving with a component along the surface are experiencing a different potential than are those moving perpendicular to the surface. Naively, but illustratively, one might imagine the potential function of Fig. 1 to be dependent on the angle between an axis of vibration and the surface in such a way that the energy for separation would be higher as that angle became smaller. In the limit of vibration entirely parallel to the surface, the potential function would be the full parabolic one, in which case no evaporation would occur.

Thus the result given by Eq. (14) makes it relatively easy to associate surface regions several Ångströms in thickness with generally observed values of vaporization coefficients. It also indicates that the evaporating atoms escape directly from the outermost atomic layer.

Another aspect of evaporation theory which might be discussed under the present heading is the equilibrium theory of absolute reaction rates. To apply this theory⁽¹²⁾ to the present problem, one postulates

that the antecedent equilibrium situation involves the bulk solid (reactant), the vapor (product), and, in addition, a bounding surface phase (activated complex) between the two bulk phases.⁽¹⁾

A surface is frequently discussed as a separate phase in such cases as one in which the condensed phase is so highly dispersed that the surface free energy makes a significant (and hence measurable) contribution to the total free energy of the condensed material.⁽¹³⁾ Here it is required as a logical element of the theory apart from its numerical contribution. Such a numerical contribution will, of course, be of central importance to the present problem. It seems clear that properties of this surface region will be as important as those of either bulk phase in the determination of the values of the nonequilibrium coefficients. Since such a surface "phase" is also an element in the discussion in Section IV, in which an irreversible thermodynamic treatment is attempted, it will be well to discuss it a little further.

It was mentioned that there are circumstances when it is convenient to treat the surface as a separate phase. Actually, however, this treatment consists in the assessment of the excess (positive or negative) value of thermodynamic functions in the surface region of the solid phase over what they would be were these functions constant in value throughout that phase. (As pointed out by Ricci,⁽¹⁴⁾ for instance, constancy of physical and chemical properties is not of overriding importance for the definition of a phase as long as continuous rather than abrupt changes occur.) The surface region is not a separate phase in the sense of the Phase Rule and cannot be counted, nor can its area be counted as an independent variable, when one is trying to determine the possible number of phases coexisting in equilibrium. This is most easily seen, for instance, by remembering that the "vapor pressure" of a highly dispersed condensed phase is higher than when the same amount of material has the minimum possible area. Thus a dispersed (condensed) phase will revert to a collected one.

Although the surface region is not a true phase, it is still, of course, discussable within the framework of equilibrium theory⁽¹³⁾ - there will be some equilibrium variation in density normal to the surface, for instance. It has been tacitly assumed, when the theory of absolute reaction rates has been applied to this problem, that this equilibrium surface condition is not altered by maintaining the bounding vapor in a nonequilibrium condition. Such an assumption does not seem to be imperative, however.⁽¹⁵⁾ In the same vein, the applications of this theory to date have involved exclusively the attribution of gas-like properties to the surface. It would seem more likely that the fundamental properties which determine the value of a (non-unit) vaporization coefficient would be as closely related to those of the bulk solid as to those of the vapor.⁽¹⁵⁾ The avoidance of the treatment of surfaces in the present context by the assignment of solid-like properties to them has probably been caused by the traditionally closer and more detailed agreement between theory and experiment in the case of vapors.

Certainly, further progress ought to be more rapidly obtainable, however, by the treatment of the surface as a Debye solid, say, with properties (the Debye function, density, and zero-point energy) numerically near those of the bulk material. The properties of the vapor phase will still be a necessary part of the treatment, of course. It is necessary to know the final states as well as the initial ones, and equations analogous to Eq. (12)-(14) will appear. The point is that a solid-like rather than a gas-like surface might provide a more realistic description of the initial states.

The authors must add here, however, that they hesitate to change too many variables at once. As a consequence, in the example which is used below to illustrate the application of irreversible thermodynamics to this problem, the more familiar model of a gas-like surface will be kept. To do so does not exhibit as much back-pedaling as might first seem to be the case, however. The absolute reaction rate theory and irreversible thermodynamics are related to each other in the same way as equilibrium statistical mechanics and reversible thermodynamics. They should be complementary rather than competitive.

IV. IRREVERSIBLE CHARACTER OF EVAPORATION

It is not particularly surprising that equilibrium thermodynamics or any theory based upon it cannot yield any information about vaporization or condensation coefficients. Hopefully, one may attempt to adapt the theory of the absolute reaction rates by the arbitrary introduction of a partition function which will describe the rate process. If this is done, however, one should make certain that the form of the activated complex is not incompatible with the process it is designed to describe. For example, the concept of evaporation occurring via a two-dimensional gas with the evaporation coordinate identified as the reaction coordinate is difficult to reconcile with the original derivation of the Maxwellian distribution of velocities, and yields an expression which is not entirely satisfactory.⁽¹⁶⁾ A two-dimensional gas is one for which the velocity component perpendicular to the surface is zero. How, then, does a two-dimensional gas evaporate? It appears more fruitful to recognize initially that nonequilibrium evaporation (such items as vaporization coefficients need never be introduced into a discussion of equilibrium processes) is essentially an irreversible process, to treat it thermodynamically as such, and then to use this framework as a guide for the construction of a mechanistic theory.

The situation which one seeks is not a study defined by the equilibrium condition that $\Delta S_{\text{total}} = 0$, but rather by the nonequilibrium condition that $\Delta S_{\text{total}} > 0$. In the formulation of the theory one must study most importantly a system which inherently has the latter property and not a portion of a total system at equilibrium which fulfills this condition simply because one restricts his attention only to that part of the total system.

For example, in the study of the gas effusing from a Knudsen cell one ordinarily assumes an equilibrium gas and arbitrarily derives the rate expression only for those molecules which escape out the orifice. For these, $\Delta S > 0$. But one has neglected the rest of the system, for which $\Delta S < 0$ since, by definition, the system is at equilibrium. Such a study will yield no information about vaporization coefficients.

One must recognize initially that any flow or rate is proportional to a force. The analysis outlined in this section enables one to deduce that in the present case the principal forces which must be considered are

$$\Delta(1/T) > 0 \quad , \quad (15)$$

and/or

$$\Delta(\mu/T) > 0 \quad , \quad (16)$$

in which μ is the chemical potential. Recognition of these conditions at the boundary contrasted to the condition $\Delta(\mu/T) = 0$, and the derivation of the equations which follow, constitute a phenomenological theory of evaporation.

Since the application of this theory to the process of evaporation is still in its infancy, there is a natural tendency to step only slowly away from equilibrium ideas. It is certainly true that proper differential application of the ideas lead to the ability to discuss irreversible processes within a phase. The application to the case of evaporation, however, must be made principally at the phase boundary. This application will be made without too much attention being paid to irreversible processes within the phases, such as heat flow in the condensed phase toward the boundary and particle flow in the vapor phase away from the boundary, in spite of the fact that they are necessary adjuncts to evaporation at the boundary. On the other hand, it should be remembered that if the application is made correctly, it will yield a result which is incomplete (for experimental application) but not erroneous because of the lack of consideration of processes occurring within the phases. The results will be in terms of quantities whose numerical values would have to be known at the phase boundary; in most cases these numbers would have to be inferred from values somewhere within the phases after a proper discussion of the irreversible processes which occur within the phases.

Further, as pointed out in the previous section, there presently exists an ambiguity as to the proper viewpoint of the principal rate-determining step at the phase boundary. The sort of treatment one should give this problem within the framework of irreversible thermodynamics will be illustrated with some detail, but with a simple model, for the case of a rate-determining step between a surface gas and the vapor. The sorts of changes in the treatment that would have to be made for a preferable but more difficult model will be indicated in the Summary, Section V.

If one assumes that the rates of flow are linear functions of some tentatively unspecified forces and if, for sake of generality, one assumes that the flows of such quantities as mass and heat may have a mutual influence on each other, then one can write the thermodynamic equations of motion in the form

$$J_1 = L_{11} X_1 + L_{12} X_2 \quad ; \quad (17)$$

$$J_2 = L_{21} X_1 + L_{22} X_2 \quad , \quad (18)$$

in which the J 's are the fluxes of quantities such as mass and heat, the X 's are the thermodynamic forces, and the L 's are the phenomenological coefficients. From fluctuation theory and the principle of microscopic reversibility (see References 17-19), one can prove the Onsager reciprocal relation

$$L_{12} = L_{21} \quad , \quad (19)$$

and, as a result of this relation, one finds that

$$\left(\frac{\partial J_1}{\partial X_2} \right)_{X_1} = \left(\frac{\partial J_2}{\partial X_1} \right)_{X_2} . \quad (20)$$

This equality demonstrates that $J_1 dX_1 + J_2 dX_2$ is an exact differential for irreversible processes which obey the linear Eqs. (17), (18), and (19). Hence, there exists some function f such that

$$df = J_1 dX_1 + J_2 dX_2 \quad . \quad (21)$$

Using Eqs. (17) and (18) for the J 's, one finds that

$$2f = L_{11} X_1^2 + 2 L_{12} X_1 X_2 + L_{22} X_2^2 \quad . \quad (22)$$

Therefore, at equilibrium, when J_1 and J_2 are zero, and consequently X_1 and X_2 are zero (we suppose the determinant of the L 's to be nonzero), the function f is zero. For a spontaneous process in which X_1 and/or X_2 is greater than zero, $2f > 0$. In these two respects f has the same properties as entropy; f , however, as can be seen from its units, must be a rate.

The general result of a thermodynamic discussion of irreversible processes then is that if the processes are formulated in a manner such that the rate of production or generation of entropy is written in the form^(17,19)

$$2f = \frac{dS}{dt} = \sum_k J_k X_k \quad , \quad (23)$$

in which J_k is a flux, then the X_k 's can be considered as thermodynamic forces in the sense that a flux is proportional to a force, i.e.,

$$J_k = \sum_j L_{jk} X_j \quad (24)$$

Equation (22) clearly shows that there can be a catastrophic loss of information in an attempt to understand vaporization coefficients in terms of an equilibrium theory. The rate processes are determined by the phenomenological coefficients L_{jk} and, since at equilibrium the X 's and $2f$ are zero, all information about the L 's is lost. Therefore, one must confine all discussion to a system for which $\Delta S > 0$ to understand rate processes.

Let the process of evaporation be represented by the thermodynamic system sketched in Fig. 2. The solid phase is located within a large, initially evacuated volume which contains the vapor phase. The boundary

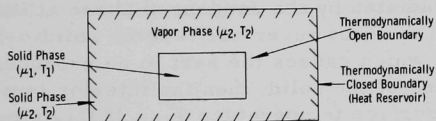


Fig. 2. Thermodynamic Representation of Evaporation

between the two phases is thermodynamically open, i.e., both energy and mass can flow across it, whereas the outer boundary is thermodynamically closed with respect to mass flow and is in contact with a heat reservoir. It is assumed that the solid phase has a uniform chemical potential μ_1 at a temperature T_1 and, similarly, the vapor phase has a uniform chemical potential μ_2 at temperature T_2 . Furthermore, the thermodynamically closed boundary is lined with the solid phase also having a chemical potential μ_2 at temperature T_2 . Since the discussion here concerns itself with the most important aspects of the nonequilibrium evaporation process occurring at the thermodynamically open boundary, it is assumed that the volume containing the vapor phase (μ_2, T_2) is sufficiently large such that the particles leaving the solid phase (μ_1, T_1) would strike the closed boundary (μ_2, T_2) many times, if they did not condense on the first impact, before returning to the solid phase (μ_1, T_1). By means of this artifice one need not be concerned with the arrival of particles at the open boundary with a chemical potential and temperature different from those at the closed boundary. It will also be assumed, of course, that while the evaporation process is nonequilibrium, it is steady state; temperatures are constant, and the concern is only with the steady transfer of matter from the solid phase (μ_1, T_1) to the vapor phase (μ_2, T_2). The total time rate of change of entropy in this system is equal to the sum of the rate at which entropy flows into it and the rate at which it is generated within it. Thus,

$$\frac{dS}{dt} = \frac{d_e S}{dt} + \frac{d_i S}{dt} \quad (25)$$

in which $d_e S/dt$ represents the flow of entropy from the environment (heat reservoir) and $d_i S/dt$ represents the production of entropy within the system. Having set up the problem, one can refer to several sources(17-19) for the method of solution. A principal difference between the present case and those in the sources cited is the existence of the large potential energy difference, the heat of vaporization, between the two regions of interest.

In time dt an increment of heat, $d_e Q$, is absorbed by the solid phase (μ_1, T_1), which, according to the first law of thermodynamics, can be distributed as an increase in the energy of the solid phase and as the external work done by the system. Here no external work is done; the only work is the internal work of expansion upon vaporization, and the only effect is an increase in internal energy of the total system. The assumed characteristics of the system are such that this energy increase will be associated only with the promotion of material from the solid phase to the vapor phase and not with any increase in energy of the material in the vapor phase. The net heat absorbed, $d_e Q$, is the difference between that ($d_e Q_1$ say) produced by electrical energy and that ($d_e Q_s$) radiated by the condensed phase at its surface (which by definition flows into the heat reservoir). If the solid phase (μ_1, T_1) is heated by any method which causes the heat to be produced and, hence, absorbed within the interior of the solid, then the interior temperature T_{1i} will be greater than the surface temperature T_{1s} . If this situation exists, then one can write that the rate at which entropy flows into the system is

$$\frac{d_e S}{dt} = \frac{1}{T_{1i}} \frac{d_e Q_i}{dt} + \frac{1}{T_{1s}} \frac{d_e Q_s}{dt} \quad , \quad (26)$$

with $T_{1i} > T_{1s}$. For small rates of evaporation and high temperatures, $d_e Q_s$ will be very nearly the same as $-d_e Q_i$, so that $d_e S/dt < 0$. If on the other hand, the solid is heated by radiant heat, T_{1i} is not likely to be greater than T_{1s} , but the exact relation between them in this case has not been studied sufficiently to be clear.(20)

The above discussion constitutes that which is to be made here with relation to irreversible processes within a phase. That is, $d_e S/dt$ will be closely related to the process of heat conduction from the actual point of input to the phase boundary. To discuss the principal part of the problem, one must now center attention on the evaluation of $d_i S/dt$. If one considers the thermodynamic relations between the two open subsystems, the solid and vapor phases, he must recognize that both energy and mass can flow across the open boundary. Two general equations can be applied to each phase. The conservation of energy for this part of the system assumes the form

$$dE = d_i \phi - p_i dV \quad , \quad (27)$$

in which $d_i\phi$, is the energy transfer which results from both heat and mass transfer in time dt . Recognizing specifically that mass can flow between the phases, one also writes the general equation

$$dS = \frac{dE}{T} + p \frac{dV}{T} - \frac{\mu}{T} dn \quad , \quad (28)$$

in which μ is the chemical potential of the chemical species of which the phases are composed.

The application, now, of these two equations, Eqs. (27) and (28), to each of the two phases in order to find the total rate of entropy production within the system leads to

$$\frac{d_i S}{dt} = \frac{1}{T_{1S}} \frac{d_i \phi_1}{dt} + \frac{1}{T_{2S}} \frac{d_i \phi_2}{dt} - \frac{\mu_1}{T_{1S}} \frac{dn_1}{dt} + \frac{\mu_2}{T_{2S}} \frac{dn_2}{dt} \quad . \quad (29)$$

But since there can be no accumulation of either mass or energy at the interface, one writes that

$$\frac{d_i S}{dt} = \frac{d_e Q}{dt} \Delta\left(\frac{1}{T}\right) + \frac{d_i m}{dt} \Delta\left(\frac{-\mu}{T}\right) \quad ; \quad (30)$$

i.e.,

$$-d_i \phi_1 = d_i \phi_2 = d_e Q \text{ and } -dn_1 = dn_2 \quad .$$

If the total system is assumed to be in a stationary state defined by $dS/dt = 0$, then for all cases in which $d_e S/dt < 0$ one observes that $d_i S/dt > 0$. Hence, if the condensed phase is heated electrically, as previously considered, entropy is produced within the system as a result of heat and mass flow across the thermodynamically open boundary between the two phases.

The selection of the forces, within the bounds of Eq. (23), is illustrated as follows. According to the definition of $d_e Q$, it is composed of the energy transfer associated with the net mass flow J_m plus any additional energy not so associated which would, then, have to be associated with an energy accommodation coefficient. If J_{th} represents this total flux, $d_e Q/dt$, then

$$\frac{d_i S}{dt} = J_{th} \Delta\left(\frac{1}{T}\right) + J_m \Delta\left(-\frac{\mu}{T}\right) \quad , \quad (32)$$

where [compare Eqs. (23) and (24)]

$$J_{th} = L_{11} \Delta\left(\frac{1}{T}\right) + L_{12} \Delta\left(-\frac{\mu}{T}\right) \quad ; \quad (33)$$

$$J_m = L_{21}\Delta\left(\frac{1}{T}\right) + L_{22}\Delta\left(-\frac{\mu}{T}\right) \quad (34)$$

It is intended to illustrate, by subsequent discussion of the form of the L 's, the sorts of relations and interplay that might be expected between them. It is well to emphasize first, however, a point made by de Groot.⁽¹⁷⁾ This is that the theoretical evaluation of the L 's will have to depend on kinetic assumptions about the individual materials being investigated. It is here that experience gained through use of the equilibrium theory of absolute reaction rates will be helpful.

The generalized analysis of both reversible and irreversible aspects of the evaporation process is summarized in Fig. 3. The former, corresponding to the process occurring at the thermodynamically closed boundary in Fig. 2, is represented by the upper portion of Fig. 3, whereas the latter, occurring at the thermodynamically open boundary, is illustrated by emphasizing the surface region. As indicated, there are three conceivable types of rate-determining steps that can occur at the surface. These are: (1) solid-solid, as from the bulk condensed phase to a solid-like surface; (2) solid-gas, as from the bulk condensed phase to a gas-like surface, or from a solid-like surface to a gas-like surface or the bulk vapor phase; and (3) gas-gas, as from a gas-like surface to the bulk vapor phase. The possibilities involving solid-like properties have been investigated the least and so, at the present time, appear to offer the greatest promise for progress. On the other hand, gas-like properties are more easily handled and will be used here to illustrate the procedure one would use to set up equations for experimental confirmation. That is, a reasonably detailed discussion will be given of a simple model wherein the particles of a perfect-gas-like surface pass irreversibly into a perfect gas vapor phase (Case 3 of Fig. 3). It will be assumed that there is an internal partition function of constant value, 2, in the gas-like surface and, correspondingly, an internal partition function

$$Q_i = 1 + \exp(-E_2/RT_2)$$

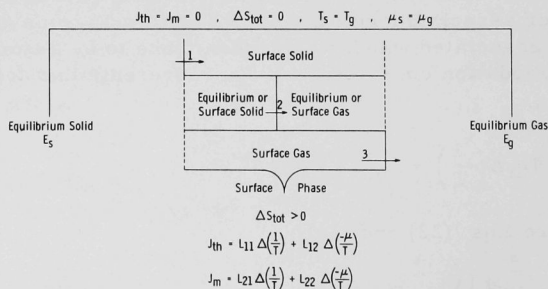


Fig. 3. Generalized Thermodynamic Analysis of Evaporation

in the gas phase.⁽²¹⁾ The translational partition function will be written in terms of the volume per mole, V_1 , for the gas-like surface but in terms of the pressure, P_2 , in the vapor phase.⁽²²⁾ The chemical potentials for the two regions will be, then,⁽²³⁾

$$\mu_1 = -RT_1 \ln [2(V_1/N_0)(2\pi mkT_1/h^2)^{3/2}] \quad ; \quad (37)$$

$$\mu_2 = -RT_2 \ln \{ [1 + \exp(-E_2/RT_2)] (kT_2/P_2) \exp(-\Delta H_0^\circ/RT_2) (2\pi mkT_2/h^2)^{3/2} \} \quad (38)$$

It will be convenient to use the saturated vapor pressure at the temperature of the surface as a base point for P_2 . This pressure is found by setting $T_2 = T_1$ in Eq. (38) and then equating the chemical potentials. The result is

$$P_s = [RT_1/2V_1][1 + \exp(-E_2/RT_1)] \exp(-\Delta H_0^\circ/RT_1) \quad (39)$$

Positive directions of flow are taken to be from the surface to the vapor phase. Thus, the Δ 's of Eq. (33) and (34) are to be found by taking the value in the vapor phase minus the value in the surface. If P_2 is set equal to $(P_s - \Delta P)$ in Eq. (38), and if $\Delta(-\mu/T)$ is formed and expanded to the first powers of $\Delta(1/T)$ and ΔP , the result is

$$\Delta(-\mu/T) = R\Delta P/P_s - [\Delta H_0^\circ + (5/2)RT_1 + \Delta H_1] \Delta(1/T) \quad , \quad (40)$$

in which

$$\Delta H_1 = E_2 \exp(-E_2/RT_1)[1 + \exp(-E_2/RT_1)]^{-1} \quad (41)$$

It is necessary now to analyze in detail the flow of mass and energy for this simple illustrative example. Let the gross outward flow of mass due to direct evaporation, $\alpha_e G_{Os}$ [see Eq. (2)], be given by

$$\alpha_e G_{Os} = \alpha_e P_s [2\pi MRT_1]^{-1/2} \quad , \quad (42)$$

where α_e is the vaporization coefficient. Similarly, if α_c is the condensation coefficient, the gross condensation rate is

$$\alpha_c G_i = \alpha_c (P_s - \Delta P) [2\pi MRT_2]^{-1/2} \quad (43)$$

It would be well to discuss, at this point, certain aspects of the simplified version of this model (Case 3 of Fig. 3) which are not necessarily inherent properties of the model. First, the vaporization coefficient used here is merely a factor that multiplies that gross flow, G_{Os} , derived with the Maxwellian velocity distribution. This means that it is independent of the velocity and direction with which a particle leaves the surface. If this is so, the vaporization coefficient of Eq. (42) cannot depend on the translational temperature of the emitted particles. It has been introduced a posteriori and, consequently, as described earlier, is of limited scope.

Secondly, the same sort of argument leads to a conclusion that the vaporization coefficient cannot depend on the internal temperature, since Eq. (42) contains the saturation (equilibrium) vapor pressure corresponding to the temperature (internal and translational) of the surface region.

Thirdly, it should be noted that there is not necessarily, in general, a complete correlation between the establishment of translational equilibrium distribution among internal states. Because of this it is possible, even in this simple example, for there to be a temperature dependence of the condensation coefficient. In fact, it will be supposed that the α_c of this version of the model is given by

$$\alpha_c = \alpha_e [1 - (AE_2/R) \Delta(1/T)] \quad (44)$$

Here, A is an unknown dimensionless coefficient; this particular form for the temperature dependence of α_c emphasizes that, were there no energy difference between internal states, this α_c would be as independent of temperature as α_e . Note also that no term involving a pressure difference is included in Eq. (44); it is assumed that α_c does not depend on a flow rate per se.

When this definition of α_c is used and when the net flow rate J_m [the difference between Eqs. (42) and (43)] is found and expanded to the first powers of $\Delta(1/T)$ and ΔP , the result is

$$J_m = (\alpha_e G_{Os}/R)(AE_2 - \frac{1}{2}RT_1)\Delta(1/T) + \alpha_e G_{Os}(\Delta P/P_s) \quad (45)$$

The thermal flow, exclusive of the radiation discussed relative to Eq. (26), is made up of two parts. One of these will be that involved in the transfer of mass and the other will involve the process generally described with the aid of "accommodation coefficients;" the latter thermal flow can occur even with no net mass flow. In connection with the first part, the discussion relative to the vaporization coefficient leads to the conclusion that the energy transfer connected with direct vaporization [Eq. (42)] is ΔH° , the equilibrium heat of vaporization of the surface material⁽²³⁾ at the temperature of the condensed phase. Because of the problems of accommodation, however, the heat transfer upon condensation is not necessarily ΔH° . Rather, this heat will be written as

$$\Delta H^* = \Delta H^\circ [1 - (B/R) \Delta(1/T) - C(\Delta P/P_s)] \quad (46)$$

Here, B is some unknown coefficient having the units of energy, whereas C is an unknown dimensionless coefficient. The net thermal flow connected with the mass flow is, then, $\alpha_e G_{Os} \Delta H^\circ - \alpha_c G_i \Delta H^*$.

Of all the particles which strike the phase boundary from the vapor side of the number

$$\mathcal{N} = (1 - \alpha_c)(P_s - \Delta P)(2\pi MRT_2)^{-1/2} \quad (47)$$

are reflected. It will be assumed that these are only partially accommodated to the surface temperature and that, in fact, Eq. (3) can be applied to the translational degrees of freedom (accommodation coefficient a) and to the internal degrees of freedom (accommodation coefficient a_i). In each case the heat flow to the gas phase will be of the form $(E_r - E_i)$.

The rate at which kinetic energy is brought up to one cm^2 of plane surface by a Maxwellian gas is $2RT_2$ times the number of moles which strike the one cm^2 per sec, where T_2 is the temperature of the gas. The result is similar, of course, for particles leaving a plane surface, provided they leave with Maxwellian characteristics. In the present case, Eq. (47) gives the number of moles of both incident and reflected particles which are of concern; it is a happenstance that \mathcal{R} is calculated with the use of the number T_2 , for instance.

If T is used as the translational temperature of the reflected and partially accommodated particles, then the thermal flow due to changes in translational energy will be

$$J_{\text{trans}} = \mathcal{R}(2RT - 2RT_2) \quad (48)$$

The use of Eq. (3), in order to put this in terms of "measurable" temperatures, gives

$$J_{\text{trans}} = 2a\mathcal{R} (T_1 - T_2) \quad (49)$$

There is, of course, a distinct difference between the kinetic energy of translation associated with one mole of gas in one cubic centimeter and the energy which is brought up to 1 cm^2 of plane surface in one second. Specifically, the numerical coefficient of temperature in Eq. (49) is associated entirely with the directional characteristics of translational motion and is not characteristic of the internal state of the particles. Therefore, it is also necessary to define an accommodation coefficient a_i for internal energy changes upon reflection such that

$$J_{\text{int}} = a_i \mathcal{R} [\Delta H_i (T_1) - \Delta H_i (T_2)] \quad (50)$$

The expansion of these thermal flow expressions to the first power of $\Delta(1/T)$ [Eqs. (49) and (50)] yields

$$J_{\text{trans}} = 2(1 - \alpha_e) a RT_1^2 G_{\text{Os}} \Delta(1/T) \quad ; \quad (51)$$

$$J_{\text{int}} = a_i (1 - \alpha_e) G_{\text{Os}} (\Delta H_i^2 / R) \exp[E_2 / RT_1] \Delta(1/T) \quad (52)$$

Thus, finally,

$$\begin{aligned}
J_{th} = & (\alpha_e G_{Os}/R) [\Delta H^\circ (AE_2 - RT_1/2 + B) + (2/\alpha_e)(1 - \alpha_e) a R^2 T_1^2 \\
& + (a_i/\alpha_e)(1 - \alpha_e) \Delta H_1^2 \exp(E_2/RT_1)] \Delta(1/T) \\
& + \alpha_e G_{Os} \Delta H^\circ (1 + C) (\Delta P/P_s) \quad . \quad (53)
\end{aligned}$$

In order, now, to determine the coefficients in Eqs. (33) and (34), Eqs. (40), (45), and (53) are to be substituted into them and coefficients of $\Delta(1/T)$ and ΔP , respectively, equated. The results are:

$$\begin{aligned}
L_{11} = & (\alpha_e G_{Os} \Delta H^\circ / R) [(1 + C)(\Delta H^\circ + 3/2 RT_1) + B + AE_2 - 1/2 RT_1] \\
& + (2a/R)(1 - \alpha_e) G_{Os} R^2 T_1^2 + (a_i/R)(1 - \alpha_e) G_{Os} \Delta H_1^2 \\
& \exp[E_2/(RT_1)] \quad , \quad (54)
\end{aligned}$$

$$L_{12} = (\Delta H^\circ \alpha_e G_{Os}/R)(1 + C) \quad , \quad (55)$$

$$L_{21} = (\alpha_e G_{Os}/R)(AE_2 + RT_1 + \Delta H^\circ) \quad , \quad (56)$$

$$L_{22} = (\alpha_e G_{Os}/R) \quad . \quad (57)$$

It is the object of this approach to impose Onsager's relations (merely $L_{12} = L_{21}$, in this case) to see what sort of results, which can be subjected to experimental test, might be obtained. If this is done here, the result is

$$C = (AE_2 + RT_1)/\Delta H^\circ \quad . \quad (58)$$

This result combines the pressure coefficient of ΔH^* and the temperature coefficient of the condensation coefficient. Inclusion of this result in a re-writing of the equations for J_{th} and J_m gives

$$\begin{aligned}
J_{th} = & [(\alpha_e G_{Os}/R)(B + AE_2 - 1/2 RT_1) + (2a/R)(1 - \alpha_e) G_{Os} R^2 T_1^2 \\
& + (a_i/R)(1 - \alpha_e) G_{Os} \Delta H_1^2 \exp(E_2/RT_1)] \Delta(1/T) \\
& + (\alpha_e G_{Os}/P_s)(\Delta H^\circ + AE_2 + RT_1) \Delta P \quad (59)
\end{aligned}$$

and

$$J_m = (\alpha_e G_{Os}/R)(AE_2 - 1/2 RT_1) \Delta(1/T) + \alpha_e G_{Os} (\Delta P/P_s) \quad . \quad (60)$$

It is not the purpose of this paper to discuss exhaustively all the implications even of this simple example but, rather, to illustrate the procedures and nature of discussion which, the authors believe, will initiate some understanding of the dynamic experiment as opposed to a static one.

An illustrative implication can be made simply, however. Consider the case where $\Delta(1/T)$ is zero. The condensation coefficient, then, equals the vaporization coefficient. Nevertheless, the term AE_2 , derived from a difference between them which depends on the existence of a temperature difference, still appears in J_{th} . Although the incident particles are, by the definition of this illustration, distributed between the two internal states in the ratio that corresponds to equilibrium at the temperature of the condensed phase, the total number striking is less than were the vapor-phase pressure equal to the equilibrium pressure. A heat flow to compensate for this deficiency in absolute number of particles is just as necessary, and goes into the same process of promoting atoms to states above the ground state, as though it were going into an adjustment of the relative population of the states because of a temperature difference.

V. SUMMARY

Methods for the consideration of the problems of vaporization and condensation have been reviewed. In particular, the methods of irreversible thermodynamics have been shown, by example, to be conducive to the generation of results that can be subjected to experimental test.

It should be re-emphasized that it is the opinion of the authors that it would be more fruitful to apply more intensive study to an extension of the work of Lennard-Jones et al.; ⁽⁴⁾ that is, one should replace the partition function used here for the surface with one related to the model discussed in Section III. It is believed that more careful application of that model would be more elucidating than would be further work along the lines of the illustrative model discussed here.

When such discussions are applied to experimental results, it should be remembered that the exact location of the rate-determining step - the one to which the irreversible thermodynamic discussion is to be applied - is, a priori, ambiguous. Lack of agreement with experiment could mean that the model should be changed; it could also mean, however, only that the numbers should be changed. Thus, with a solid-to-gas step one might get better agreement by estimating a frequency distribution for the surface than by using that applicable to the bulk material.

In this same connection, it must also be remembered that the illustrative theoretical discussion in Section III applied to the transition across the phase boundary, for instance, the $\Delta(1/T)$ was the temperature discontinuity across that boundary. It is not likely that one could determine this quantity accurately by using in it a T_1 measured in the interior of the bulk condensed phase.⁽¹⁾ Indeed, except possibly for metals, it is sufficiently likely that the particles evaporating from incandescent solids, and the light emitted therefrom, come from sufficiently different locations that the validity of using an optical pyrometer for measurement of T_1 should be examined.

The writers believe that the apparent vaporization coefficient of graphite reported by Thorn and Winslow⁽²⁴⁾ can also be explained in terms of a temperature discontinuity at the surface. From a study of the optical transmissivity of thin films one knows that the light which enters an optical pyrometer certainly does not originate at the outermost atomic layer. It is the sum of that emitted by each layer multiplied by the fraction transmitted to the surface, and certainly neither the emissivity of the surface layer nor its transmissivity is unity. It was shown earlier in the present discussion that most of the evaporating atoms, however, come from the outermost atomic layer. Therefore, the source of light employed to measure the surface temperature is not identical with the source of evaporating atoms. It is, consequently, extremely difficult to measure the significant temperature with an optical pyrometer; a similarly close examination would be expected to show it as difficult to do with a thermocouple.⁽²⁵⁾ Probably the most logical procedure here would be to measure the total number of particles and their velocity distribution.⁽²⁶⁾

Finally, the nature of vaporization and condensation coefficients should be carefully considered as to their dependence on existing distributions of particles among translational, vibrational, rotational, and electronic states. For the illustration used in this paper it was supposed that the distribution among internal states of the directly evaporating particles was the equilibrium one, but that incident particles, in equilibrium internally at a different temperature, do not accommodate upon impact. Hence, this model would have a temperature-independent vaporization coefficient but a temperature-dependent condensation coefficient. On the other hand, there was, at one time, much speculation that graphite evaporated directly into an electronic state other than the ground state.^(27,28) This phenomenon would produce a (internal) temperature-dependent vaporization coefficient which could be independent of the translational temperature.

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15. For instance, condensation coefficients are not generally listed as functions of temperature or pressure. On the other hand, Knacke and Stranski⁽¹⁾ state that the partition function of the activated complex could have any value between that of the saturated vapor and that of the condensed phase. Whether they meant to say so or not, this could mean their contemplation of a value which changes with changing experimental conditions.
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21. These particular choices of partition functions may seem at first glance strictly arbitrary. However, they are intended to introduce and illustrate in a simple manner two notions, the existence of frozen-in internal degrees of freedom in the surface phase, and the discontinuity of a given physical property (here the energy) between two phases.
22. It is at points such as this that theory and experiment will be of mutual assistance. This particular choice was made on the basis of the possibly naive idea that, as material evaporates, it leaves a phase of fixed volume and enters one of fixed pressure. The nature of such choices will affect the conclusions as to the energy flow in these irreversible processes.

23. The quantity ΔH_0° in Eq. (38) represents the energy difference between the ground states on each side of the irreversible boundary. If the respective ground states of the bulk solid and the gas-like surface are equal in energy, then this ΔH_0° becomes the heat of sublimation.
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